

Synthesis and Characterization of Water Stable η^3 -Allyl Dicarbonyl Complexes of Molybdenum(II)

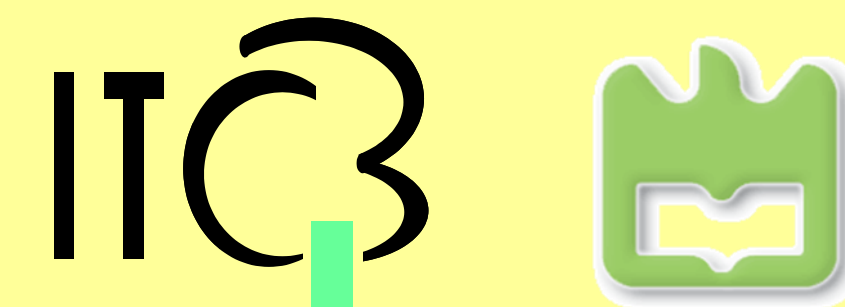
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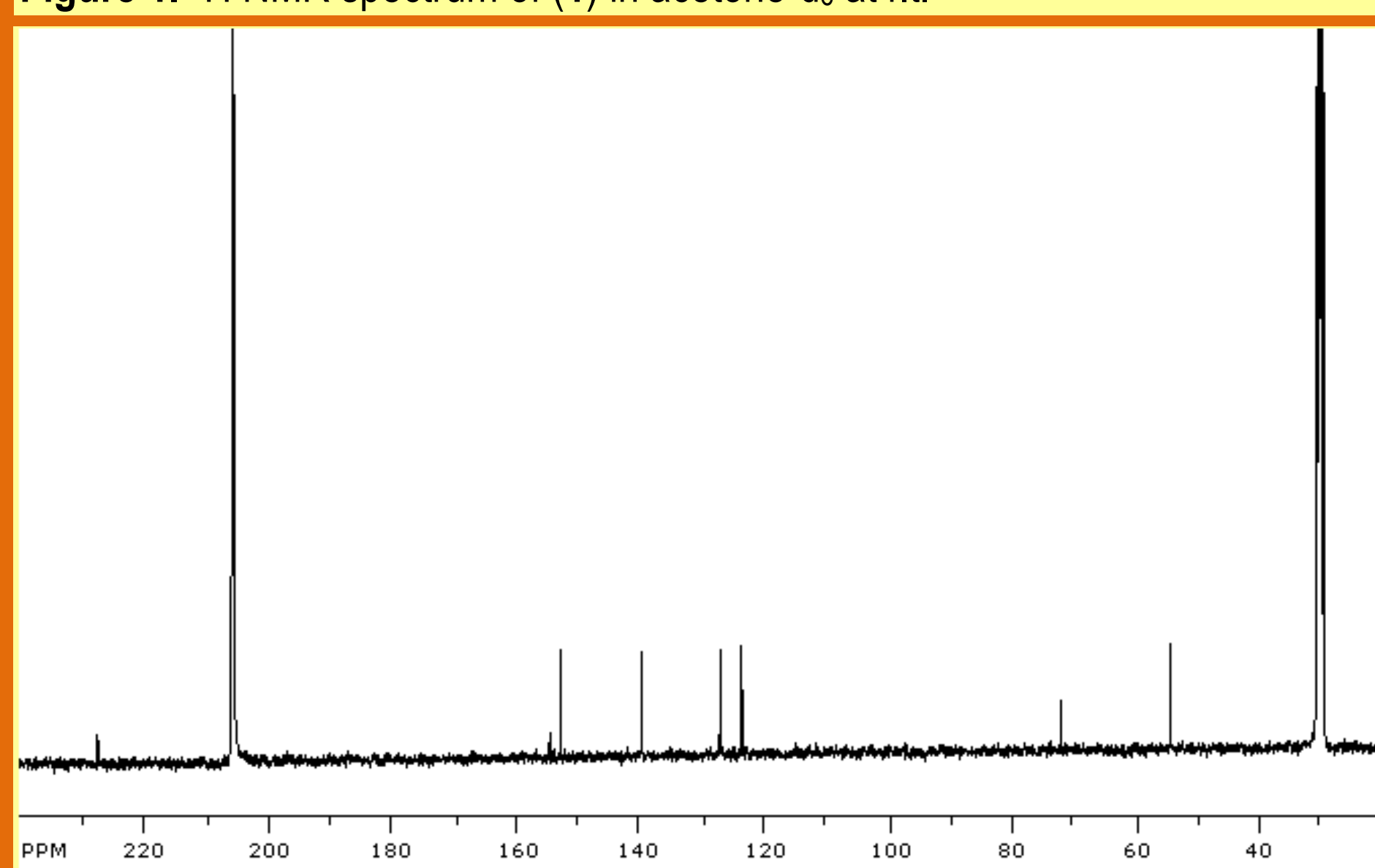
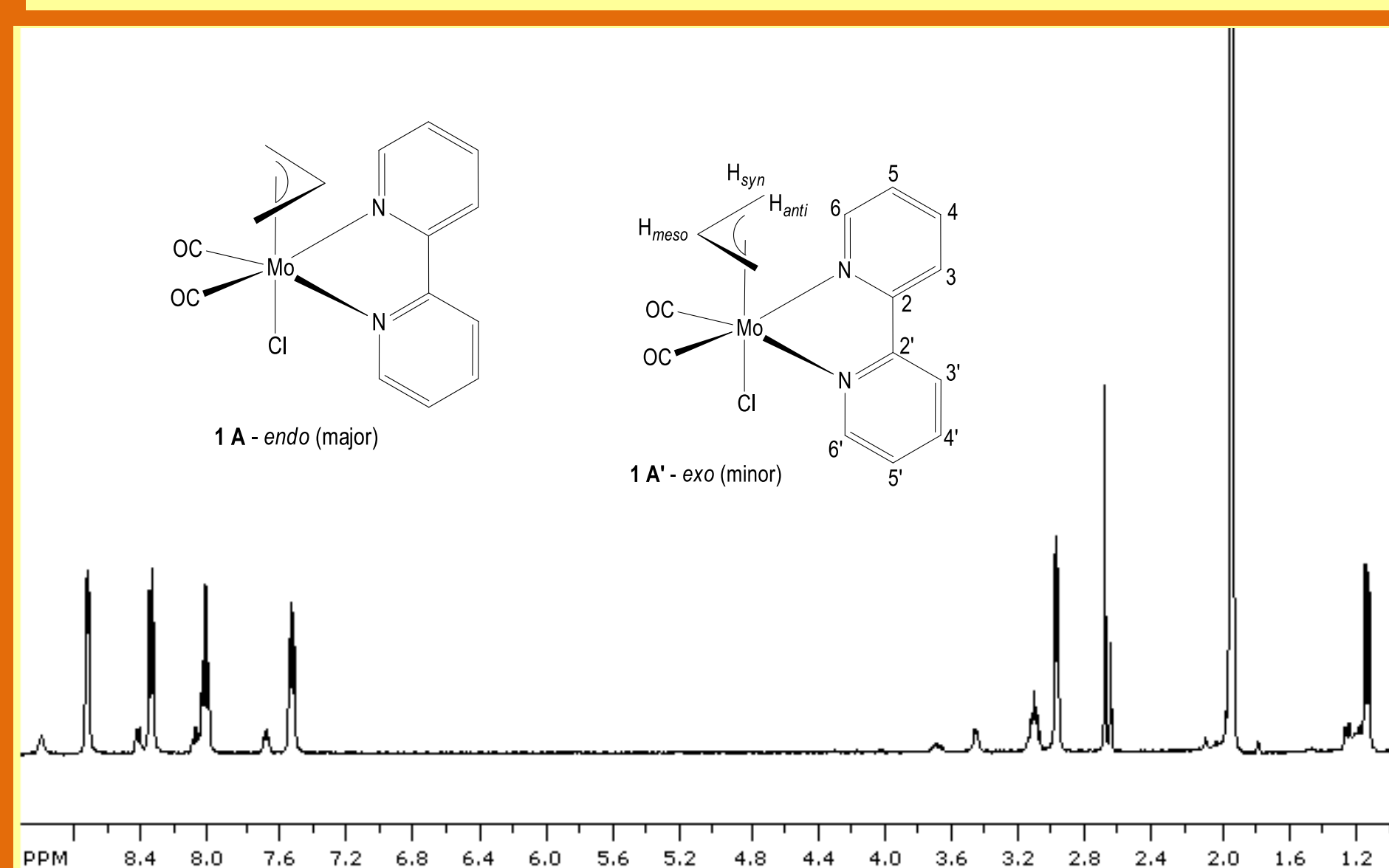
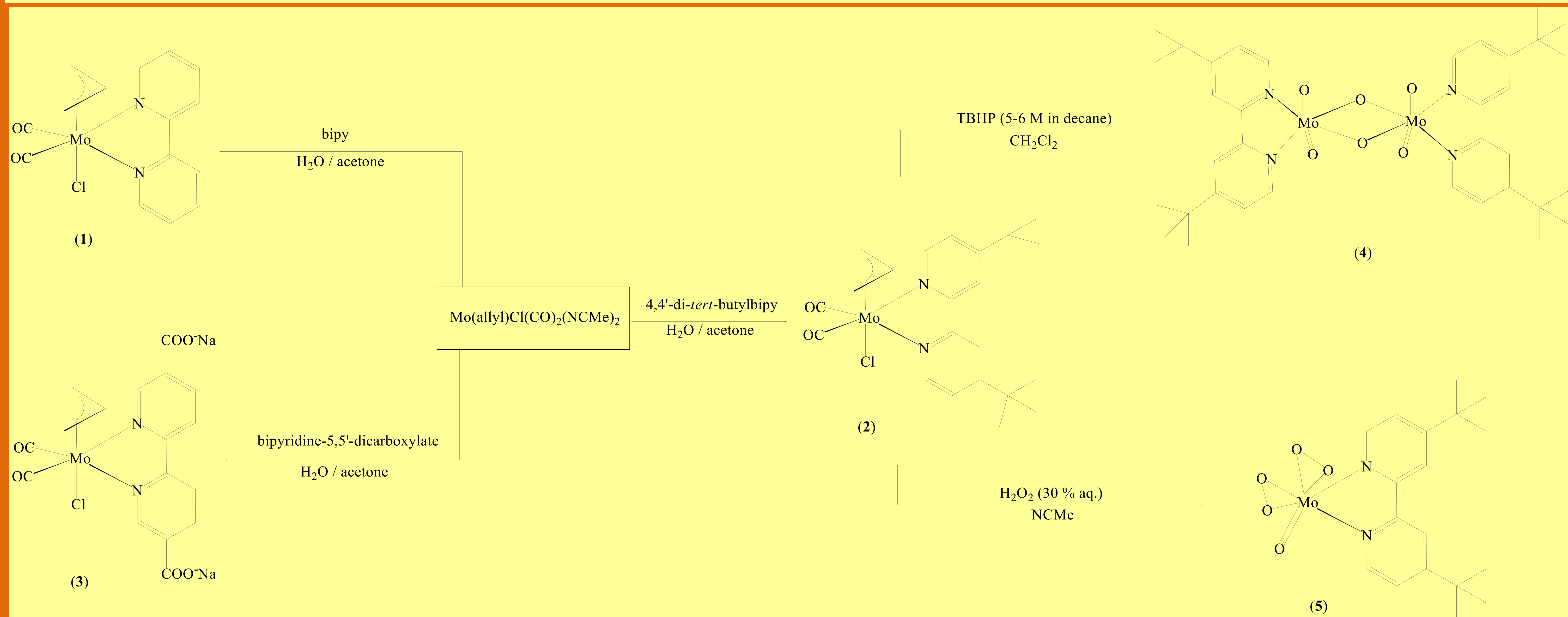
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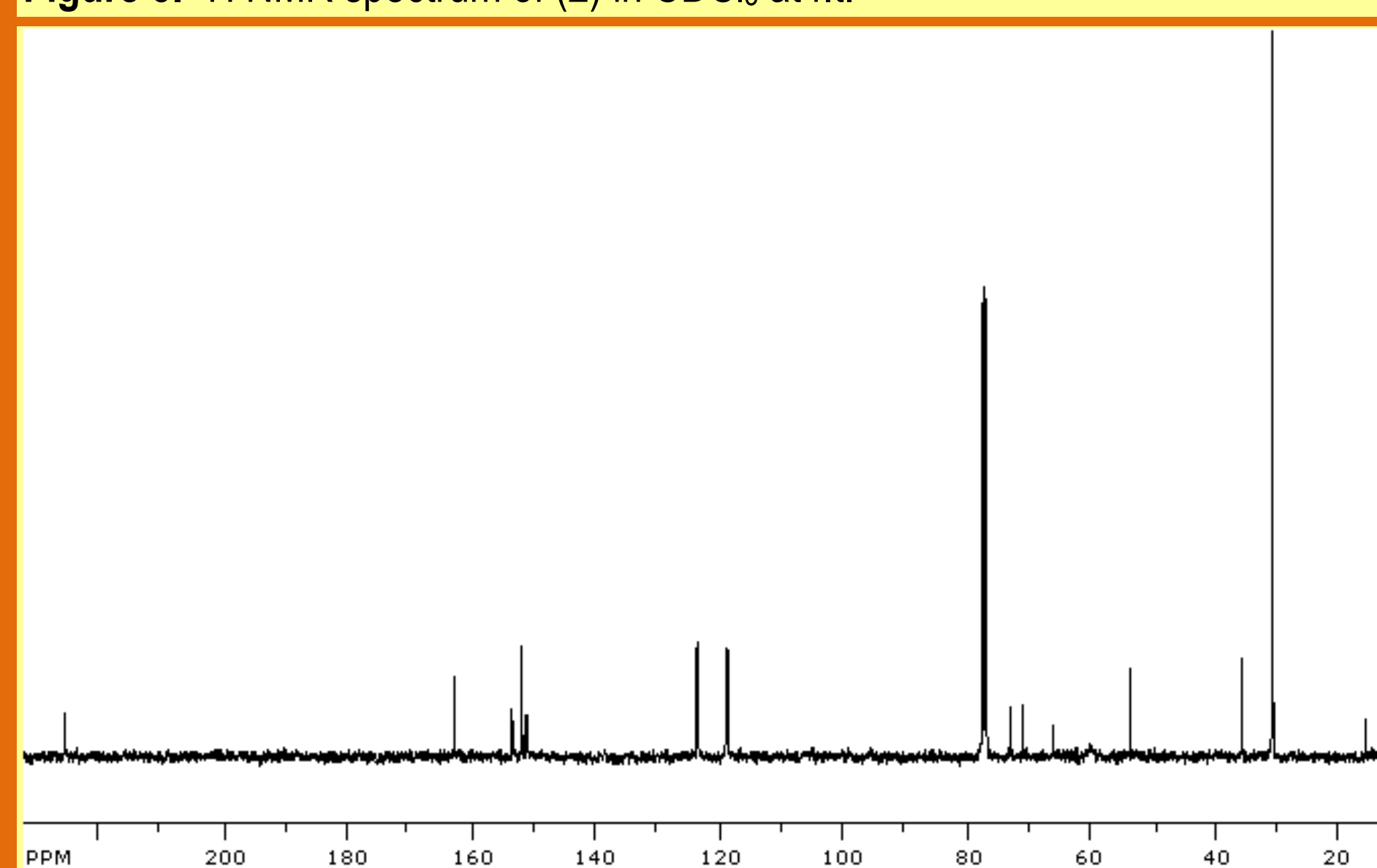
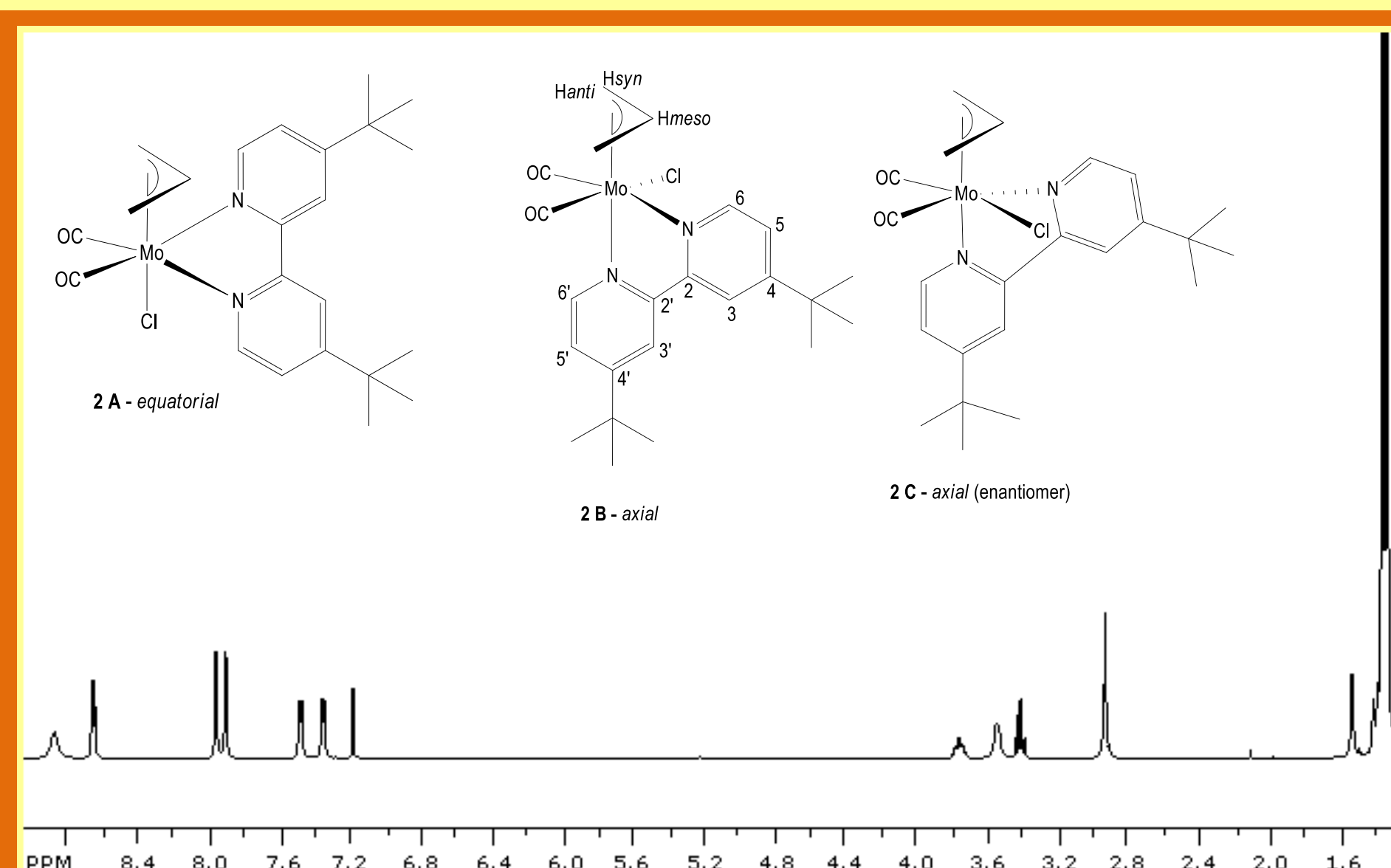
I. INTRODUCTION

The family of η^3 -allyldicarbonyl complexes of Mo(II) has been studied in coordination chemistry and catalysis, due to its facile preparation and introduction of a variety of ligands. Investigations in our laboratories have focused on new methods to prepare bent metallocene complexes of molybdenum and tungsten containing substituted cyclopentadienyl ligands or other h^5 -cyclic analogues, and we used $[\text{Mo}(\eta^3\text{-allyl})\text{Cl}(\text{CO})_2(\text{NCMe})_2]$ as starting material [1]. The acetonitrile ligands in pseudooctahedral molybdenum(II) complexes of the type $[\text{Mo}(\eta^3\text{-allyl})\text{X}(\text{CO})_2(\text{NCMe})_2]$ (X = halide) can be readily replaced by other monodentate or bidentate ligands. The resultant complexes have been successfully used as catalysts or catalyst precursors for imine aziridination, oxidation of triphenylphosphine with molecular oxygen, allylic alkylations, and recently for the oxidation of olefins [2].

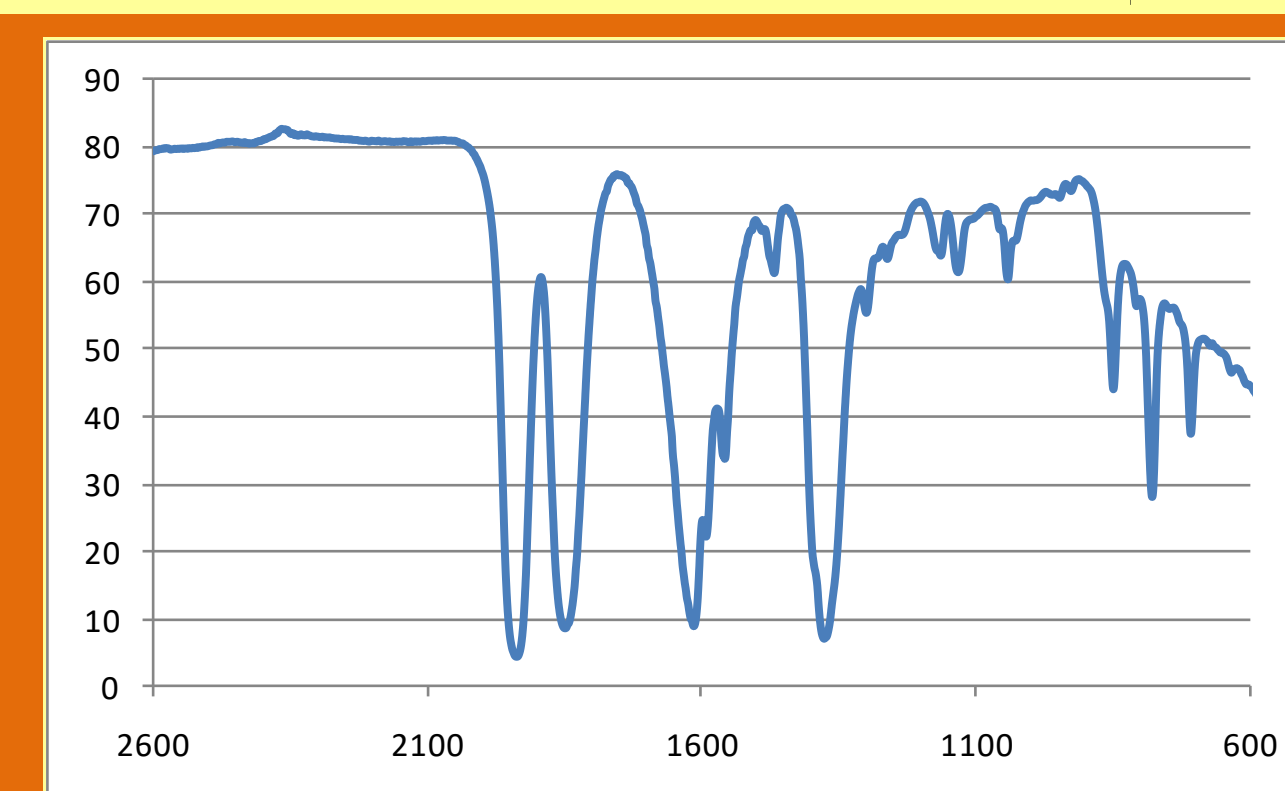
Here we report the aqueous syntheses of complexes $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{L})]$ [L = 2,2'-bipyridine (**1**), 4,4'-di-*tert*-butyl-2,2'-bipyridine (**2**), 2,2'-bipyridine-5,5'-dicarboxylate (**3**)] and their oxidative decarbonylation reactions. Complexes **1-3** have been characterized by FTIR, NMR (including COSY and HMQC) and EA.



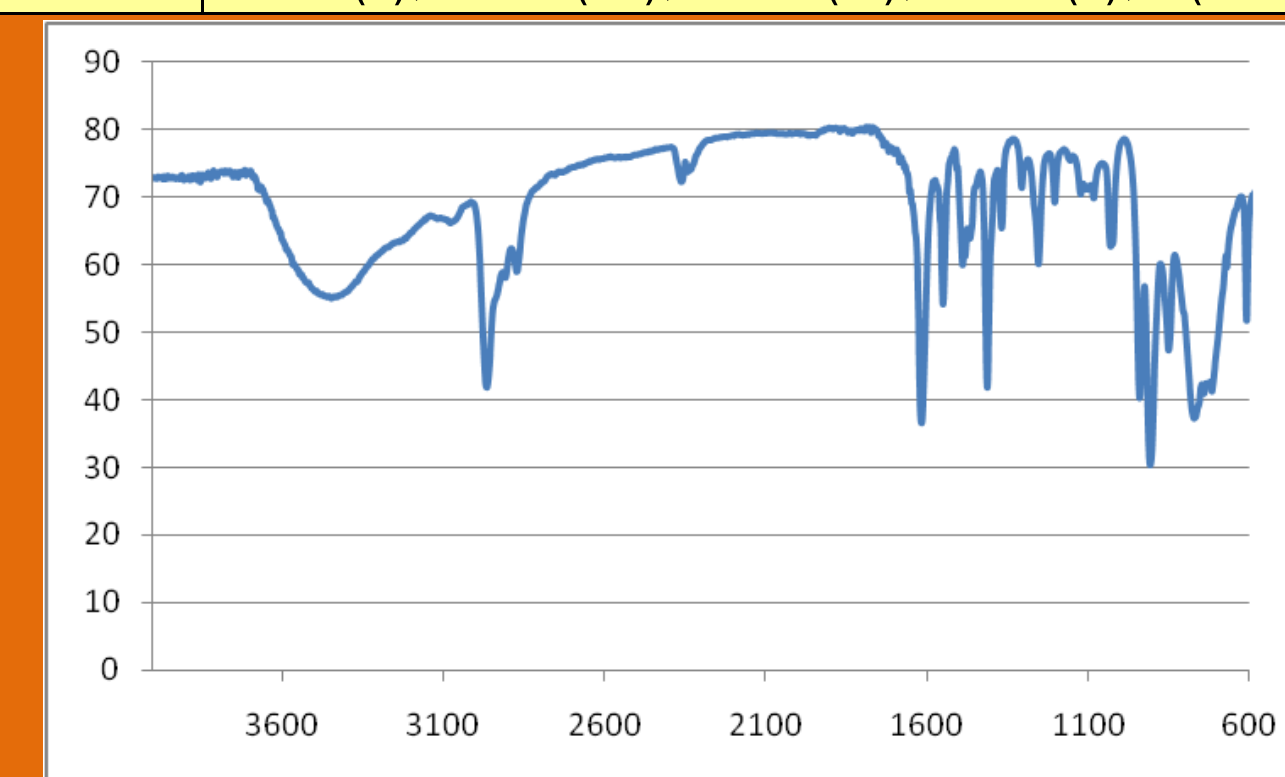
Complexes (1) and (3): Each isomer has only three allyl signals in the ^1H NMR and the two terminal carbon atoms of the allyl are equivalent in the ^{13}C NMR. Both isomers are therefore symmetrical (with bipy ligand in an equatorial position, *trans* to the two carbonyls).



Complex (2): Two sets of signals for both the di-*tert*-butylbipy and the allyl ligands are observed in the NMR spectra at r.t., corresponding to isomer **A** (symmetric) and isomers **B** and **C** (asymmetric enantiomers), as reported in the literature.³



Complex	IR (cm^{-1})
1	1938 (s), 1838 (s), $\nu(\text{CO})$ 1601 (m), 1615 (m), $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$
2	1943 (s), 1852 (s), $\nu(\text{CO})$ 1615 (m), 1547 (w), $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$
3	1938 (s), 1847 (s), $\nu(\text{CO})$ 1615 (s), 1592 (sh), 1561 (m), 1378 (s), $\nu(\text{COO}^-)$



Complex	IR (cm^{-1})
4	1614 (m), 1550 (w), $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ 939 (s), $\nu_{\text{sym}}(\text{Mo}=\text{O})$, 907 (s), $\nu_{\text{asym}}(\text{Mo}=\text{O})$ 771 (s), 744 (s), 711 (sh), $\nu(\text{Mo}-\text{O}-\text{Mo})$
5	1618 (m), 1550 (w), $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ 948 (s), $\nu_{\text{sym}}(\text{Mo}=\text{O})$ 874 (sh), 862 (s), $\nu(\text{O}-\text{O})$

CONCLUSIONS

This study reports the synthesis and characterization of η^3 -allyldicarbonyl molybdenum(II) complexes **1-3** and their oxidation reactions. The results reveal the potential application of these complexes in aqueous catalysis (which is presently being investigated), due to their high stability in water.

REFERENCES

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